

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 83302271.8

 (51) Int. Cl.³: **B 65 D 1/02**
B 29 C 17/07, B 29 D 23/03

(22) Date of filing: 21.04.83

(30) Priority: 22.04.82 JP 67780/82

 (43) Date of publication of application:
 02.11.83 Bulletin 83/44

 (84) Designated Contracting States:
 CH DE FR GB IT LI NL

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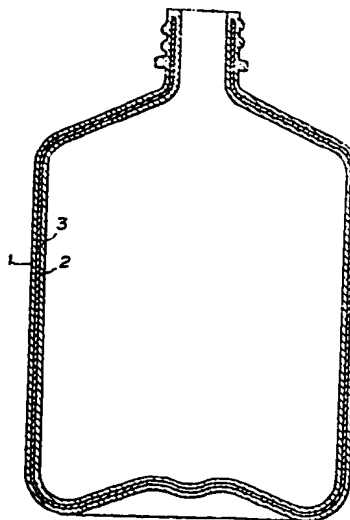
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(64) Bottle-shaped container.

(67) A hollow blow-moulded bottle-shaped container of a biaxially oriented mixture resin material comprising a polyethylene-terephthalate resin and a xylene group-containing polyamide resin, wherein the mixture resin material contains 5 to 50% of xylene group-containing polyamide resin to the polyethylene terephthalate resin. In this container, inner and outer surface layers of the container are formed of the polyethylene terephthalate resin, and the intermediate layer of the container is formed of the mixture resin material. In this manner, the gas barrier property of the container can be enhanced.

FIG. 1



"Bottle-shaped Container"

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This invention relates to a hollow blow-molded bottle-shaped container of a biaxially oriented polyethylene terephthalate resin.

A polyethylene terephthalate resin, hereinafter referred to as "PET", has a variety of excellent properties and characteristics. In order to effectively perform the excellent properties and characteristics of the PET, a bottle-shaped container of the PET is mostly biaxially oriented without exception.

10 Although the conventional hollow blow-molded bottle-shaped container of the biaxially oriented PET effectively performs a variety of properties and characteristics as described above, the container does not always sufficiently exhibit a gas barrier property.

15 In order to supplement the insufficient gas barrier property of the bottle-shaped container of the PET, it is heretofore considered to provide a hollow blow-molded bottle-shaped container of a biaxially oriented PET having a multilayer structure layer including in combination a layer
20 formed of a synthetic resin material incorporating excellent gas barrier property and a layer formed of the PET. However, the adhering strength between the layer formed of a material having an excellent gas barrier property and the layer formed of the PET is weak or insufficient because of the difference
25 of cooling shrinkage factors at a molding time between the layer formed of the material having excellent gas barrier property and the layer formed of the PET and of insufficient compatibility, bonding strength and reaction strength between the material having excellent gas barrier property and the PET.

Thus, the mechanical strength of the bottle-shaped container is not only insufficient, but also gas escaped from the content of the container such as, for example, a carbon dioxide gas is accumulated between the layer formed of the material
5 having excellent gas barrier property and the intermediate layer formed of the PET as its drawbacks.

In other words, when a preformed injection molded piece is covered with a surface layer in which both inner and outer
10 surfaces of an intermediate layer formed of a material having high gas barrier property have been covered with the PET, the surface layer and the intermediate layer are generally bonded relatively strongly in the state of the preformed injection
15 molded state. However, when the preformed piece is further blow-molded to biaxially orient the preformed piece into a bottle-shaped container, the bonding strength between the surface layer and the intermediate layer becomes extremely weak due to the difference of the degrees of orientations
20 between the surface layer and the intermediate layer of the bottle-shaped container.

Accordingly, the carbon dioxide gas penetrated into the inner surface layer is readily accumulated between the inner surface layer and the intermediate layer as described above.
25 In this manner an exfoliation between the inner surface layer and the intermediate layer not only occurs over the entire bottle shaped container, but also the body of the container tends to largely swell, since the body of the container should endure against the internal pressure thus produced of the container merely by the outer surface layer and the intermediate layer due to the internal pressure, due to the internal pressure of the container, resulting in remarkable deterioration in the external

appearance of the bottle-shaped container as a merchandise.

A resin material which has excellent gas barrier property generally has a drawback such that the material is whitened in contact with water content. When a gap is formed between
5 the inner surface layer and the intermediate layer of the bottle-shaped container as described above, the intermediate layer is whitened due to the water content which is penetrated even in a very small amount into the gap formed between the inner surface layer and the intermediate layer, thereby
10 causing a difficulty in the loss of a transparency of the bottle-shaped container.

Accordingly, an object of the present invention is to provide a hollow blow-molded bottle-shaped container of a biaxially oriented polyethylene terephthalate resin which
15 can eliminate all the aforementioned drawbacks and disadvantages of the conventional bottle-shaped container and which can maintain extremely high bonding strength between a surface layer and an intermediate layer of the container while remaining a gas barrier property.

20 Another object of the present invention is to provide a hollow blow-molded bottle-shaped container of a biaxially oriented polyethylene terephthalate resin which does not cause an exfoliation between the surface layer and the intermediate layer.

25 Yet another object of the present invention is to provide a hollow blow-molded bottle-shaped container of a biaxially oriented polyethylene terephthalate resin which can incorporate extremely high mechanical strength.

Still another object of the present invention is to

provide a hollow bottle-shaped container of a biaxially oriented polyethylene terephthalate resin which can simply control the temperature at the blow-molding time.

Still another object of the invention is to provide a
5 hollow bottle-shaped container of a biaxially oriented polyethylene terephthalate resin which can maintain high transparency even with the surface layers and the intermediate layer.

The above and other related objects and features of the
10 invention will be apparent from a reading of the following description of the disclosure found in the accompanying drawings and the novelty thereof pointed out in the appended claims.

Fig. 1 is a view showing a preferred embodiment of a
15 hollow bottle-shaped container of a biaxially oriented PET according to the present invention;

Fig. 2 is a view showing another preferred embodiment of the bottle-shaped container having two-layer structure including an outer layer formed of the mixture material of
20 the PET and xylene group containing polyamide resin and an inner layer formed of the PET; and

Fig. 3 is a view showing still another preferred embodiment of the bottle-shaped container having two-layer structure including an outer layer formed of the PET and an inner layer
25 formed of the material containing the mixture resin material of the PET and xylene group-containing polyamide resin.

The present invention will now be described in more detail with reference to the accompanying drawings.

A hollow blow-molded bottle-shaped container having excellent gas barrier property of a biaxially oriented mixture resin material without a multilayer structure will be first described as a preferred embodiment of the present invention.

This bottle-shaped container is blow-molded by a biaxial orientation with a mixture resin material which includes a PET and a xylene group-containing polyamide resin. The mixture resin material contains 5 to 30% by weight of xylene group-containing polyamide resin to the PET.

The gas barrier property of the bottle-shaped container thus prepared is performed by the operation of the xylene group-containing polyamide resin mixed at the ratio of 5 to 30% by weight to the PET. The higher the mixture ratio of the xylene group-containing polyamide resin to the PET is in this range, the higher the gas barrier property of the bottle-shaped container becomes.

This xylene group-containing polyamide resin is one of synthetic resin materials having the highest gas barrier property, has excellent physical property maintaining resistance against the content contained in the bottle-shaped container and another physical property similar to that of the PET at the molding temperature.

If the mixture ratio of the xylene group-containing polyamide resin is, however, excessively high such as large than 30% by weight to the PET, the wall structure of the bottle-shaped container becomes a laminated foil structure, thereby causing a trend of occurring an exfoliation between the foil layers of the bottle-shaped container. Thus, the mechanical strength such as the wear resistance and the

internal pressure resistance against the content contained in the container are abruptly deteriorated, and the moldability of the bottle-shaped container is largely aggravated.

Therefore, when a bottle-shaped container in which a
5 content liquid is hermetically contained in the bottle-shaped container thus formed and not so required for high gas barrier property is blow-molded, it is preferred to mold the bottle-shaped container with a mixture resin material which is mixed with approx. 5 to 10% by weight of the xylene
10 group-containing polyamide resin to the PET. On the other hand, when a bottle-shaped container in which the liquid is contained in the container required for high gas barrier property is blow-molded, it is preferred to mold the bottle-shaped container with a mixture resin material which is
15 mixed with the xylene group-containing polyamide resin of as high as possible within 30% by weight to the PET in the degree for not deteriorating the mechanical strength of the wall of the bottle-shaped container to be blow-molded.

An example of the measured values relative to the gas
20 barrier property of the bottle-shaped container will be listed below.

When a bottle-shaped container having 0.45mm of wall thickness of the body is molded only with 37g of the PET, the penetrated quantity of oxygen through the bottle-shaped
25 container was 0.0180 cc per day. When a bottle-shaped container thus molded with a mixture resin material which was mixed with 20% by weight of xylene group-containing polyamide resin to the PET, the penetrated quantity of oxygen through the bottle-shaped container was 0.0001 cc per day.
30 It was clear that the bottle-shaped container molded only

with the mixture resin material which was thus mixed with the xylene group-containing polyamide resin exhibited very high gas barrier property.

When the penetrated quantities of carbon dioxide gas of both the bottle-shaped containers thus molded were measured under the pressurized state with the conditions of the same bottle-shaped containers only with the PET and with the mixture resin material as above, the content of the carbon dioxide gas in the bottle-shaped container was reduced by 23.3% in the case that the bottle-shaped container molded only with the PET was allowed to stand for 60 days at 4°C of the temperature of the atmosphere. On the other hand, the content of the carbon dioxide gas in the bottle-shaped container was reduced only by 14.8% in the case that the bottle-shaped container molded with the mixture resin material which contains 20% by weight of xylene group-containing polyamide resin to the PET in the case that the bottle-shaped container thus molded was allowed to stand for 60 days at 4°C of the atmosphere.

From the above experiments, it became clear that the bottle-shaped container thus molded with the above mixture resin material provided high gas barrier property even to the content of carbon dioxide gas in the bottle-shaped container.

With respect to the reasons that the bottle-shaped container of the invention thus molded exhibits high gas barrier property as described above, a variety of factors can be considered as follows: From the fact that when the mixture ratio of the xylene group-containing polyamide resin to the PET is excessively increased, it is considered

that the wall structure of the bottle-shaped container thus
molded is progressively converted into laminated foil
structure so that an exfoliation between the laminated foils
tends to occur, the xylene group-containing polyamide resin
5 mixed with the PET acts to arrange the molecular array of
the PET in multilayer foils and to strengthen the bonding
between the molecules of the PET forming the respective layers,
thereby forming the wall structure of the bottle-shaped
container in a multilayer structure, with the result that
10 the high gas barrier property can be performed.

As described above, the xylene group-containing polyamide
resin serves to arrange the molecules of the PET in laminar
state and to strengthen the bonding between the molecules of
the PET, but to also weaken the bonding strength between
15 the molecules forming the respective layers and hence the
molecules between the layer. Accordingly, when the mixture
ratio of the xylene group-containing polyamide resin is
excessively large, an exfoliation between the layers of the
bottle-shaped container tends to occur, thereby deteriorating
20 the machanical strength of the bottle-shaped container,
and since the respective layers of the bottle-shaped container
are molded along the orienting direction of the blow-molding,
the moldability of the bottle-shaped container is aggravated.

A bottle-shaped container molded with a mixture resin
25 material which is mixed with the xylene group-containing
polyamide resin in the PET in a multilayer structure layer
according to another embodiment of the present invention will
now be described.

As shown in Fig. 1 the bottle-shaped container with
30 this multilayer structure layer is formed with inner and

outer surface layers 1 and 2 formed on the overall surfaces including both inner and outer surfaces of the bottle-shaped container, and with an intermediate layer 3 of the state covered on both the surface layers 1 and 2 in a multilayer 5 wall structure. The surface layers 1 and 2 are formed of the PET, and the intermediate layer 3 is formed of a mixture resin material of the PET and the xylene group-containing polyamide resin.

The mixture ratio of the xylene group-containing polyamide 10 resin to the PET forming the above intermediate layer 3 is in a range of 5 to 50% by weight of the xylene group-containing polyamide resin to the PET, and preferably 10 to 30% as well as most preferably 20%. In the case of this bottle-shaped container with the multilayer wall structure, the mixture 15 ratio of the xylene group-containing polyamide resin can be increased as compared with the bottle-shaped container with a single layer formed of the above synthetic resin since the inner and outer surface layers of the bottle-shaped container are covered with the PET.

20 According to the experiments, it was confirmed that the penetrated quantity of oxygen gas of the bottle-shaped container molded with the material which was mixed with 20% by weight of the xylene group-containing polyamide resin could be reduced to 1/10 of that of the bottle-shaped container 25 molded only with the PET single layer, and the penetrated quantity of carbon dioxide gas thereof could be reduced to 1/2 of the latter bottle-shaped container.

A method of molding a bottle-shaped container with the above multilayer wall structure can be considered in a 30 variety of processes. Generally, it is preferred that

a preformed injection-molded piece of a bottomed cylindrical shape of wall structure having first layers to become the surface layers 1 and 2 and a second layer to become the intermediate layer 3 is injection-molded by a sandwich molding method and the preformed piece thus molded is then blow-molded by a biaxial orientation into a bottle-shaped container.

When the preformed piece is injection-molded by the sandwich molding method, the thickness of the intermediate layer 3 can be arbitrarily controlled and set by setting suitably the viscosity of the resin material to form the intermediate layer 3 to the PET to form the surface layer 1.

However, it is advantageous at the point of improving the moldability of the preformed piece to increase the viscosity of the resin material to form the intermediate layer 3 larger than that of the PET to form the surface layers 1 and 2.

According to the present invention as described above, the bottle-shaped container has the surface layers 1 and 2, and the intermediate layer 3, the surface layers 1 and 2 are formed of the PET, and the intermediate layer 3 is formed of the mixture resin material which is mixed with the xylene group-containing polyamide resin in the PET. Therefore, since the PET is contained in both the surface layers 1, 2 and the intermediate layer 3, the surface layers 1, 2 and the intermediate layer 3 can be integrally fusion-bonded, whereby exfoliation between the surface layers and the intermediate layer no longer occurs.

Since the molding temperatures of the PET and the xylene group-containing polyamide resin are extremely similar, the bottle-shaped container with the surface layers and the

intermediate layer can be preferably molded.

Further, since the PET and the xylene group-containing polyamide resin forming the intermediate layer 3 are merely mixed, the physical properties of the xylene group-containing
5 polyamide resin are not varied, with the result that the intermediate layer 3 can exhibit very high gas barrier property due to the presence of the xylene group-containing polyamide resin.

Fig. 2 shows still another preferred embodiment of the
10 bottle-shaped container according to the present invention. This bottle-shaped container has a two-layer structure which contains an inner layer 4 formed of the PET and an outer layer 5 formed of a mixture resin material which is mixed with the PET and the xylene group-containing polyamide
15 resin. The mixture ratio of the xylene group-containing polyamide resin with the PET in the bottle-shaped container of this embodiment is preferably in the same manner as that of the embodiment exemplified in Fig. 1 in a range of 5 to 50% by weight of the xylene group-containing polyamide resin
20 to the PET.

Fig. 3 shows still another preferred embodiment of the bottle-shaped container according to the invention. This bottle-shaped container has, on the other hand, an inner layer 6 formed of a mixture resin material which
25 is mixed with the PET and the xylene group-containing polyamide resin and an outer layer 7 formed of the PET in a two layer structure, contrary to the relationship in Fig. 2.

As described above, the bottle-shaped container with the multilayer wall structure thus constructed exhibits
30 very high gas barrier property and extremely high bonding

strength between the surface layers and the intermediate layer. Therefore, mechanical strength of the bottle-shaped container of the invention can be enhance. Even if the layers of the bottle-shaped container employs different resin materials, the temperature of molding the bottle-shaped container can be simply controlled. Since the xylene group-containing polyamide resin has relatively high transparency, the bottle-shaped container having high transparency can be provided.

Claims

1. A hollow blow-moulded bottle-shaped container characterised in that at least part thereof - for example, a layer (3, 5, 6) - comprises a mixture of polyethylene terephthalate resin and a xylene group-containing polyamide resin.
5
2. A hollow blow-moulded bottle-shaped container according to claim 1, characterised in that the mixture of resin material comprises 5 to 50% by weight of xylene group-containing polyamide resin.
- 10 3. A hollow blow-moulded bottle-shaped container according to claim 1 or claim 2 comprising inner and outer surface layers (1, 2) and an intermediate layer (3), characterised in that the surface layers (1,2) are formed of a polyethylene terephthalate resin, while the intermediate layer (3) is
15 formed of a mixture of polyethylene terephthalate resin and a xylene group-containing polyamide resin.
4. A hollow blow-moulded bottle-shaped container according to claim 1 or claim 2 comprising an
20 inner layer (4) and an outer layer (5), characterised in that the outer layer (5) is formed of a mixture of polyethylene terephthalate resin and a xylene group-containing polyamide resin, and the inner layer (4) is formed of polyethylene terephthalate resin.
- 25 5. A hollow blow-moulded bottle-shaped con-

- tainer according to claim 1 or claim 2 comprising an inner layer (6) and an outer layer (7), characterised in that the outer layer (7) is formed of polyethylene terephthalate resin, and the inner layer (6) is
- 5 formed of a mixture of polyethylene terephthalate resin and xylene group-containing polyamide resin.
6. A hollow blow-moulded bottle-shaped container according to any preceding claim, characterised in that the mixture of resin material comprises 10 to 30% by
- 10 weight of xylene group-containing polyamide resin.

FIG. 1

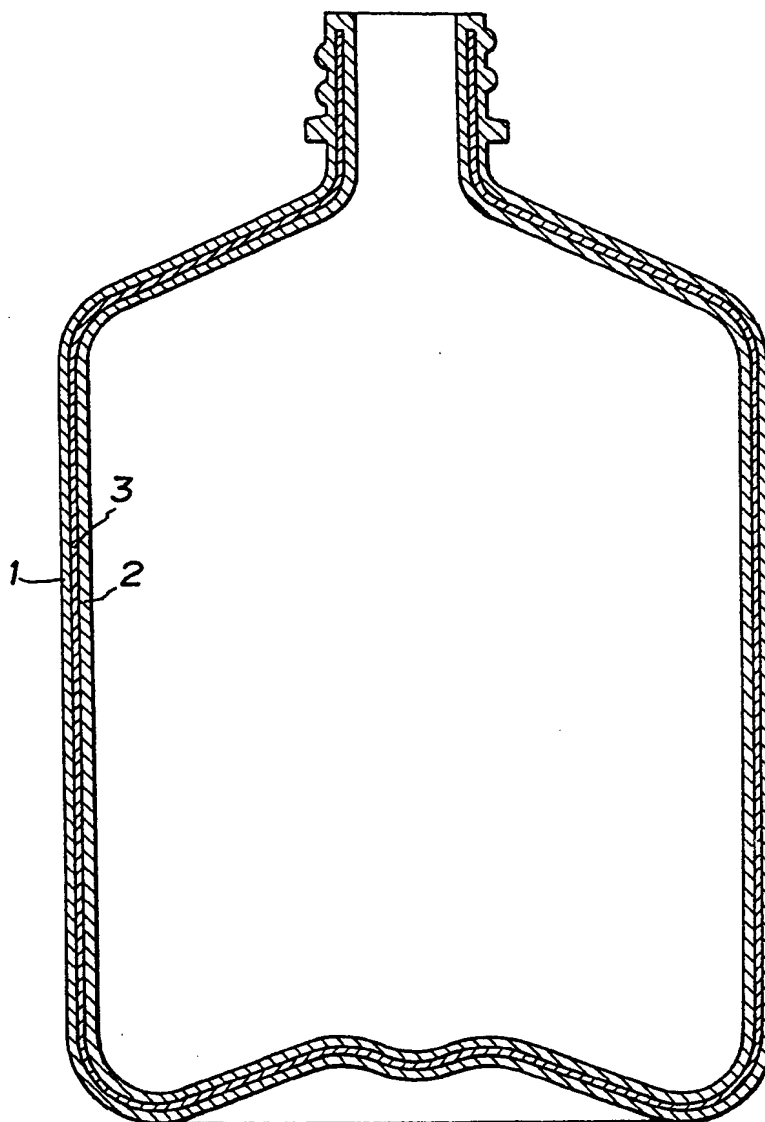


FIG. 2

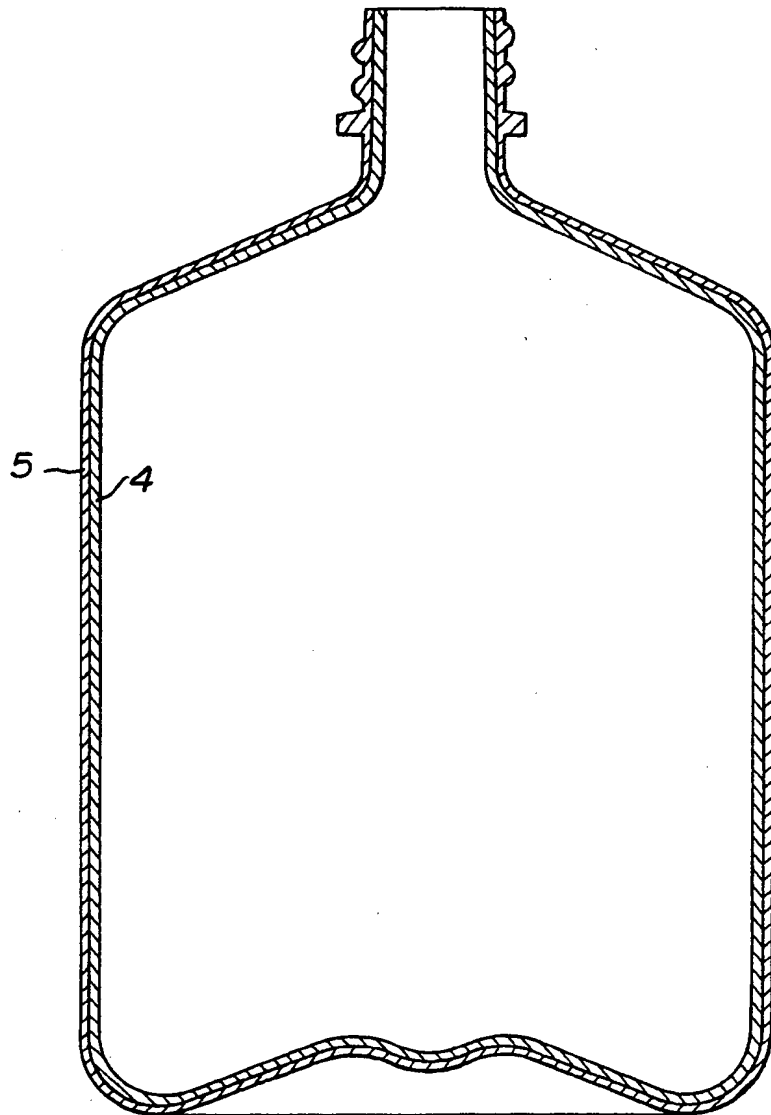


FIG. 3

